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SAMPLING ARTIFACTS AND POTENTIAL TRANSPORT OF METAL COLLOIDS SAN FERNANDO VALLEY BASIN, CALIFORNIA

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ABSTRACT

Groundwater transport of metals has historically been thought to occur via dissolved species. Accordingly, sampling procedures have typically included filtering to remove particulate matter. Recently, it has been suggested that metals may be transported within an aquifer as filterable, colloidal-sized material. Monitoring wells recently installed in the San Fernando Valley Basin indicate that the concentration of some metals is dependent upon filtering. When filtered and unfiltered samples of groundwater indicate the presence of significantly different concentrations of metals, it can be difficult to determine whether unfiltered data reflect the presence of mobile colloids or are simply "sampling artifacts" unique to the well bore area and sampling system. Metals data obtained from the San Fernando Valley Basin suggest significant sampling artifacts are present in unfiltered samples. Metals data in samples filtered with a 0.45-μm filter most closely resemble nearby production well data, and are considered representative of natural groundwater conditions.

KEY WORDS

Metals, Colloids, Filtering, Groundwater Sampling, Sampling Artifacts

INTRODUCTION

Metals transport within aquifers has historically been thought to occur via dissolved constituents. Accordingly, standard metals sampling techniques have typically included filtering groundwater samples with a 0.45-μm or finer filter to remove particulate matter; the particulate matter was thought to have been introduced from the well casing and well bore and therefore would not reflect the amount of metals transported through the aquifer. Such filtering is recommended by EPA (1986). Recently, interest has been expressed in collecting unfiltered samples to characterize the total amount of "mobil" metals within an aquifer as it has suggested that metals

may be transported over large distances within an aquifer as filterable, colloidal-sized material (Puls and Barcelona 1989a; 1989b). Colloids are extremely small particulates, typically defined as having an upper size limit of 1 μm (Mills and others, 1991). To accurately assess the concentration of "mobile" metal species within an aquifer, it has been recommended that water samples be collected in an unfiltered state, or that at most a 5-μm filter be used (Puls and Barcelona 1989a; 1989b). Colloids appear to be most readily transported through fractured rock and clean sand and gravel aquifers; questions remain regarding the degree of colloid transport through silt- and clay-bearing aquifers (Mason and others, 1992).

BACKGROUND

A total of 87 RI monitoring wells have been installed in the San Fernando Valley Basin (SFVB) as part of ongoing EPA RI/FS studies. Groundwater samples obtained from these wells have been analyzed for potential organic and metal contaminants. Results of metals analyses indicate that observed metal concentrations are at least partially dependent upon filtering methods. The metals data obtained in the SFVB to date could have significant implications for risk assessments for future remediation.

When filtered and unfiltered samples of groundwater provide significantly different results it can be difficult to determine whether unfiltered data reflect the presence of mobile colloids or "sampling artifacts" related to the sampling process and that are unique to the well bore area (see, for example, Puls and Barcelona, 1989a; and, Hall and Luttrell, 1990). These artifacts include drilling fluids that have invaded the formation and corrosion products that form in and near the well bore and sampling systems. Iron oxyhydroxides are a common corrosion product within a well bore environment and can strongly adsorb metals. Care must be taken to prevent these materials from entering the sample, or else the sample will not be representative of aquifer conditions.

To help address potential problems associated with sampling artifacts, the following recommendations regarding monitoring well construction, development, and sampling procedures have been made (Puls and Barcelona 1989a; 1989b):

- Use of drilling mud should be avoided; if used it must be properly developed out of the well prior to sampling.

- Gravel pack material should be properly selected to allow good hydraulic communication with the aquifer but prevent fine-grained material from entering the well.

- Purge and sample rates should not exceed well development pumping rates. Bladder pumps should be used for purging and sampling and the rate kept as close to the natural discharge rate of the aquifer as possible (stated to commonly range from about 0.05 to 0.15 gpm). These low discharge rates are designed to avoid disturbance of fine-grained material and/or precipitates that may have entered and/or formed in the well and subsequently accumulated in the well casing.

- Air contact should be minimized during sample collection because changes in Eh and pH can affect colloid formation, which in turn can affect metal concentrations.

- Unfiltered samples should be collected, or samples filtered with at most an in-line 5-μm filter. Collection of samples for geochemical speciation modeling should include use of a 0.1-μm or finer in-line filter.

- Disturbance of the well casing and bottom sediments with water level sounders and sampling equipment must be avoided.

Hall and Luttrell (1990) have investigated the effect of purge volume with respect to several parameters, including pH, conductivity, temperature, total iron, and turbidity. Results of their work indicate that temperature, conductivity, and pH stabilize relatively quickly (within 3 to 5 well volumes), but that turbidity and iron concentrations may continue to decrease for an extended period of time (over 100 well volumes). This pattern is recurrent upon separate sampling events, indicating that the effects of well purging are short-lived. The authors state that "If any of the measured turbidity were due to colloidal transport within the aquifer, the turbidity data would be expected to stabilize at a level representing 'natural' transport of particulate matter" (Hall and Luttrell, 1990). The authors state that because turbidity did not stabilize during pumping, particulate materials related to the well bore environment ("sampling artifacts") were always present within discharge water. This work suggests that collection of unfiltered samples may not provide results indicative of insitu metals concentrations even after extended well purging because of the presence of these sampling artifacts. The authors state that time-series analysis of site-specific metals and/or other parameters should be conducted to identify appropriate purge volumes.

SAN FERNANDO VALLEY BASIN DATA

Monitoring Well Construction Techniques and Sampling Methods. The SFVB RI monitoring wells were installed using the mud rotary technique. The wells are constructed using 4-inch diameter stainless-steel wire-wrap well screen, typically using about 20 feet of well screen. The well screen is connected to 10 feet of blank stainless-steel casing, with 4-inch diameter low-carbon steel casing extending to ground surface. Recent field work has indicated the presence of abundant iron-oxides at the top of the casing.

Development of relatively shallow water table monitoring wells in the basin included bailing with a 3-inch diameter bailer, followed by swabbing with a single-action surge block for about 30 to 60 minutes. Accumulated sediment was bailed from the bottom of the well, and a submersible pump was then installed and pumped at a rate between about 7 to 10 gpm until turbidity was "low" with only "minor amounts of fines." During pumping development the pump was raised and lowered throughout the entire length of well screen. Accumulated sediment was bailed from the bottom of the well after pumping. The pH, color, and electrical conductivity of the water were monitored during pumping. Development was considered complete when these parameters had stabilized and at least 3 well volumes had been purged. Development of deeper wells that experienced excessive drawdown was conducted with high-velocity water jetting. Development

of these deeper wells was considered complete when pH, "apparent turbidity", and electrical conductivity were stable and at least 3 well volumes had been purged. Turbidity measurements were obtained visually or with a turbidimeter.

Fourteen (14) of the shallow monitoring wells were equipped with both dedicated submersible pumps for purging, and bladder pumps for sampling. The submersible pumps within these wells are designed to have flow rates between about 5 and 10 gpm, with a maximum of about 15 gpm. These wells were previously sampled by installing and purging with a temporary submersible pump, and then collecting groundwater samples with a bailer. Filtering of bailed samples was typically performed using off-line 1.2-μm canister filters.

Monitoring Wells Metals Data. Available RI monitoring well metals data collected to date are summarized in Table 1. As indicated in Table 1, 9 metals have been detected at concentrations that exceed primary MCLs or secondary standards: 9 in unfiltered samples; 6 in samples filtered with a 1.2-μm filter; and, 0 in samples filtered with a 0.45-μm filter. The number of wells exhibiting concentrations of metals exceeding MCLs appears to decrease with decreasing filter size, although relatively few wells have been sampled with a 0.45-μm filter (Table 2). Samples from 7 wells were obtained sequentially using no filter, a 1.2-μm filter, and a 0.45-μm filter to better evaluate effects of filtering (Table 2). Based upon "filterability", the metals have been placed into 1 of 3 groups (Table 2):

- **Group 1: No concentration difference between unfiltered and filtered samples.** This group includes calcium, magnesium, sodium, and potassium. These constituents appear to be present solely within a dissolved phase that readily passes through the filters.

- **Group 2: Concentration is less in the filtered samples relative to unfiltered samples.** This group includes iron, manganese, aluminum, chromium, barium, vanadium, copper, lead, zinc, and silver. These constituents appear to be present both within a relatively coarse solid phase that is readily filterable with a 1.2-μm filter, within a colloidal phase that may or may not be filterable with the 0.45-μm filter, and within a dissolved phase.

- **Group 3: Variable concentration.** This group includes arsenic, antimony and selenium. The concentration of these elements exhibit no readily distinguishable relationship with filtering.

Production Wells Metals Data. To better evaluate which type of RI monitoring well samples (unfiltered, 1.2-μm filtered, or 0.45-μm filtered) best represent metal concentrations in groundwater, results of metals analyses from production wells in selected well fields within the SFVB were compiled and compared with nearby RI monitoring well data. Due to prolonged pumping, these production wells should not be affected by well bore/sampling artifact effects, and samples from these wells should reflect the amount of metals transported by the local groundwater system. The monitoring wells are located between about 100 feet to one mile from the production wells, and have been out of service for several years due to concentrations of TCE and/or PCE in exceedence of the 5 ppb MCL. The production wells were sampled without

TABLE 1. Monitoring well metals data summary.

Compound	Unfiltered Wells Sampled	Wells Detected	Range (ug/l) Low	High	Filtered: 1.2 um Wells Sampled	Wells Detected	Range (ug/l) Low	High	Filtered: 0.45 um Wells Sampled	Wells Detected	Range (ug/l) Low	High	EPA MCL ug/l		Number of Wells with MCL Exceedences Unfilt	1.2 u	0.45 u
Arsenic	48	27	1	440	82	29	1	16	10	0	-	-	50	PM	13	0	0
Barium	7	7	69	358	45	45	32	283	10	10	56	248	1,000	PM	0	0	0
Cadmium	48	7	6	33	88	1	5	5	10	0	-	-	10	PM	5	0	0
Mercury	48	14	0	47	82	25	0	8	10	0	-	-	2	PM	8	2	0
Selenium	48	6	1	19	82	17	1	91	10	4	1	4	10	PM	2	3	0
Silver	48	3	9	18	82	16	5	19	10	1	6	6	50	PM	0	0	0
Chromium	48	29	11	160	69	12	6	1,200	10	0	-	-	50	PM	19	4	0
Copper	48	32	5	2,100	69	5	5	60	10	4	4	4	1,000	SC	1	0	0
Iron	7	7	8,720	31,800	45	44	20	3,780	10	10	12	227	300	SC	7	4	0
Lead	48	25	1	56	82	12	1	200	10	3	1	3	50	SC	2	2	0
Manganese	7	7	86	307	45	45	4	1,520	10	10	3	41	50	SC	7	8	0
NOTES:	PM -Primary MCL																
	SC- Secondary MCL																

filters, using bottles that contain preservatives. Monitoring wells in this area are screened at many of the same intervals as the production wells. Because of the close proximity of the wells and similarity of screened intervals, and providing that sampling artifacts effects are not present, RI monitoring wells within each individual subarea should exhibit similar metals concentrations as the nearby production wells.

Metals concentration data for samples obtained from production wells most closely resemble filtered data from the RI monitoring wells (Table 2). Results of unfiltered samples from nearby RI monitoring wells indicate relatively high concentrations of metals (commonly in exceedence of one or more primary and/or secondary MCL), and are *not* reflective of production well data. Therefore, unfiltered data are *not* considered to be representative of the metals content of local insitu groundwater.

Elevated concentrations of metals within the unfiltered samples are probably related to sampling artifacts. The sampling artifacts may have several possible origins. Most importantly, during installation of the temporary submersible pump used for purging it is likely that rust and other material inside the casing well was disturbed, resulting in suspension of particulate matter within the well; introduction of the bailer caused additional disturbance. Particulates that became suspended in the water within the well casing at this time may have been incorporated into the bailed samples, digested by the acid preservative in the sample bottle, leading to results that do not accurately reflect insitu groundwater conditions.

DISCUSSION AND CONCLUSIONS

Available data suggest that sampling artifacts have influenced results of metals sampling in the SFVB. Data provided in Table 2 indicate high concentrations of iron in all the unfiltered samples of groundwater, with iron concentrations decreasing by 1 to 2 orders of magnitude upon filtering with a 1.2-μm filter. This drastic decrease in iron concentration upon relatively coarse filtering appears to be reasonably attributable to sampling artifacts related to the presence of iron-rich particulates/colloids in and near the well bore. This interpretation is supported by the fact that production wells in the area do not have reported high concentrations of iron. The presence of an abundant and relatively coarse iron phase may indicate the presence of corrosion products within the well and sampling system. Because iron readily adsorbs other metals, the relatively elevated concentrations of other Group 2 metals in the unfiltered samples may reflect adsorption of these metals onto iron-rich particulate/colloidal phases, or may have formed their own colloidal phases (Table 2). In this case, metals present in these phases would not be indicative of concentrations transported through the aquifer. Similar reasoning may be applicable to results of 1.2-μm versus 0.45-μm filter samples, indicating that colloids related to sampling artifacts may be present in the 1.2-μm filtered samples (Table 2). However, more work needs to be performed to better define this issue. In addition, the relatively high concentration of aluminum in unfiltered samples suggests that clay or other aluminum-rich minerals may have contaminated these samples.

As stated above, the apparent problems with sampling artifacts may have several possible origins. Most importantly, during installation of the temporary submersible pump used for sampling it is likely that rust and other material inside the casing well was disturbed, resulting

TABLE 2. Production well and monitoring well metals data.

Well	Sample Date	Filter Size	GROUP1				GROUP2						GROUP3						
			Ca	Mg	Na	K	Fe	Mn	Al	Cr	Ba	V	Cu	Pb	Zn	Ag	As	Sb	Se
EPA MCL							300	50	20	50			1,000	50		50	50		10
Production wells:																			
G-14	May-89	Unfilt.	-	-	-	-	<20	14	<100	<5	-	-	<20	2	10	-	<1	-	1
G11	May-89	Unfilt.	-	-	-	-	<20	14	<100	<5	-	-	<20	2	7	-	<1	-	<1
CS-45	Mar-84	Unfilt.	-	-	-	-	-	<10	-	<10	-	-	<20	<10	10	-	<10	-	8
CS-45	Jul-81	Unfilt.	-	-	-	-	-	<10	-	<10	-	-	<20	<10	10	-	<10	-	3
CS-46	Mar-84	Unfilt.	-	-	-	-	-	<10	-	<10	-	-	<20	<10	10	-	<10	-	4
CS-46	Jul-81	Unfilt.	-	-	-	-	-	30	-	<10	-	-	<20	<10	30	-	<10	-	3
G-1	May-89	Unfilt.	-	-	-	-	<20	14	<100	<5	-	-	<20	2	27	-	<1	-	<1
G-2	May-89	Unfilt.	-	-	-	-	<20	14	<100	<5	-	-	<20	2	6	-	<1	-	<1
G-12	May-89	Unfilt.	-	-	-	-	<20	14	<100	<5	-	-	<20	5	12	-	<1	-	1
G-15	May-89	Unfilt.	-	-	-	-	<20	14	<100	<5	-	-	<20	2	7	-	<1	-	<1
Monitoring wells near wellfield:																			
CS-C03-100	Apr-91	Unfilt.	112	43	57	3.8	28,100	286	8,520	29	358	43	15	5.1	78	15.6	3.1	39	2.5
CS-C03-100	Apr-91	1.2 um	109	38	55	1.7	65	21	0	0	248	16	0	0.0	14	7.5	0.0	36	1.1
CS-C03-100	Apr-91	0.45 um	111	38	55	1.8	44	16	1,610	0	248	17	0	0.0	16	6.6	0.0	0	4.2
CS-C03-325	Apr-91	Unfilt.	48	13	33	4.4	23,200	295	4,000	24	127	23	10	2.1	112	9.1	0.0	0	1.0
CS-C03-325	Apr-91	1.2 um	43	10	33	3.5	113	21	0	0	74	9	0	0.0	33	0.0	1.0	0	0.0
CS-C03-325	Apr-91	0.45 um	43	10	32	3.2	57	31	0	0	71	5	4	0.0	0	0.0	0.0	0	0.0
CS-C03-465	Apr-91	Unfilt.	65	14	30	5.0	31,800	307	3,840	24	147	26	14	2.0	154	9.8	0.0	0	0.0
CS-C03-465	Apr-91	1.2 um	51	12	29	3.5	141	23	0	0	68	5	0	0.0	0	0.0	1.9	0	0.0
CS-C03-465	Apr-91	0.45 um	54	12	30	3.7	66	27	0	0	69	6	4	0.0	5	0.0	0.0	0	0.0
CS-C03-550	Apr-91	Unfilt.	45	9	109	4.6	12,800	135	470	0	71	11	49	4.4	89	0.0	1.0	0	0.0
CS-C03-550	Apr-91	1.2 um	38	9	104	4.2	105	29	0	0	58	7	0	0.0	8	0.0	1.4	0	0.0
CS-C03-550	Apr-91	0.45 um	39	9	108	4.4	93	41	0	0	56	6	4	0.0	0	0.0	0.0	0	0.0
CS-C04-290	Mar-91	Unfilt.	63	15	28	4.3	12,200	218	3,050	14	126	11	5	6.5	48	0.0	1.4	0	1.1
CS-C04-290	Mar-91	1.2 um	62	14	29	4.2	20	32	0	0	82	0	0	0.0	4	0.0	0.0	33	0.0
CS-C04-290	Mar-91	0.45 um	62	14	28	4.3	85	22	0	0	85	7	0	0.0	17	0.0	0.0	54	1.1
CS-C04-382	Mar-91	Unfilt.	71	14	30	3.4	8,720	96	425	0	84	8	0	1.4	28	0.0	1.2	0	1.7
CS-C04-382	Mar-91	1.2 um	64	14	30	4.7	153	16	0	0	77	5	0	0.0	4	0.0	1.2	38	1.4
CS-C04-382	Mar-91	0.45 um	67	14	31	4.7	134	16	0	0	82	0	0	3.0	5	0.0	0.0	25	1.6
CS-C04-520	Mar-91	Unfilt.	62	12	125	4.2	8,570	86	127	0	69	8	0	1.0	15	0.0	0.0	0	0.0
CS-C04-520	Mar-91	1.2 um	53	11	117	4.5	210	14	0	0	57	7	0	2.2	0	0.0	0.0	0	0.0
CS-C04-520	Mar-91	0.45 um	54	11	121	4.6	227	15	0	0	57	9	0	2.4	0	0.0	0.0	0	0.0
CS-C05-180	Mar-91	1.2 um	-	-	-	-	71	17	-	0	75	-	0	1.1	0	-	0.0	-	1.6
CS-C05-180	May-90	1.2 um	-	-	-	-	-	-	-	-	-	-	-	0.0	8	-	0.0	-	0.0
CS-C05-280	Mar-91	1.2 um	-	-	-	-	72	18	-	0	158	-	0	1.1	9	-	0.0	-	2.2
All values in ug/l																			

in suspension of particulate matter within the well; introduction of the bailer caused additional disturbance. Particulates, including colloidal sized material, that became suspended in the water within the well casing at these times may have been incorporated into the samples, thereby providing results that do not accurately reflect insitu groundwater conditions. Because of the apparent abundant presence of sampling artifacts in unfiltered samples, the 1.2-μm filter data must also be considered suspect.

Metals data from production wells located near some of the RI wells indicate generally low concentrations of metals, with all metal analytes below primary and secondary MCLs. Comparison of metals concentration data for the production wells with nearby RI monitoring wells indicates that concentrations of metals within filtered monitoring well samples are most similar to production well samples. Therefore, filtered RI monitoring well samples appear to provide the most representative metals data for insitu groundwater. Filtered metals data obtained from RI monitoring wells are generally below primary and secondary MCLs. Two observed primary MCL metals exceedences in filtered RI well samples have not been replicated.

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